

L Number	Hits	Search Text	DB	Time stamp
1	170	inspect\$3 near9 (material near2 substrate)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 12:55
2	304	(polymer near mixture) near5 substrate	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:30
3	0	(inspect\$3 near9 (material near2 substrate)) and ((polymer near mixture) near5 substrate)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 12:56
4	13	((polymer near mixture) near5 substrate) and inspect\$3	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:00
5	18	(inspect\$3 near9 (material near2 substrate)) and polymer	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:03
8	2	(surface near inspect\$3 and 356/601) and polymer	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:04
6	22	surface near inspect\$3 and 356/614	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:10
7	31	surface near inspect\$3 and 356/601	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:14
9	16	appli\$2 near ((polymer near mixture) near5 substrate)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:14
10	16	(appli\$2 near ((polymer near mixture) near5 substrate)) and (substrate or material)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:16
11	15	((appli\$2 near ((polymer near mixture) near5 substrate)) and (substrate or material)) and remov\$3	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:16
12	5	inspect\$3 near9 (polymer near mixture)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:26
13	4	(polymer near mixture) near5 (clear near substrate)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:34
14	764	inspection near15 polymer	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:35

15	5	inspection near15 (mixture near polymer)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:36
16	6	non near destructive near surface near inspection	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM TDB	2003/05/06 13:38

L Number	Hits	Search Text	DB	Time stamp
1	18	(inspection near9 polymer) and 356/\$.ccls.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:08
2	2039	(appli\$2 near2 polymer) near6 substrate	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:10
3	20394	(remov\$3 near2 polymer)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:11
4	788	(remov\$3 near2 polymer) and inspection	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:11
5	1042	(remov\$3 near2 polymer) and inspect\$3	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:12
6	13	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) and inspect\$3)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:26
7	255	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:26
8	13	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and inspect\$3	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:26
9	0	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and 356/\$.clss.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:27
10	0	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and 250/\$.clss.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:27
11	0	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and 430/\$.clss.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:27
12	0	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and 427/\$.clss.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:28
13	10	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and inspection	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:28
15	50	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and defect	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:29

16	0	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and detect near defect	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:29
14	22	((appli\$2 near2 polymer) near6 substrate) and ((remov\$3 near2 polymer) )) and detect	USPÄT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/05/06 14:29

US-PAT-NO: 4670528

DOCUMENT-IDENTIFIER: US 4670528 A

TITLE: Polymeric pyridinium ylides and  
products prepared from  
same

----- KWIC -----

FIG. 4b is a cross-sectional view of the electrodes of  
FIG. 4a with the  
protective polymer removed therefrom.

It will be seen from inspection of the polymer unit  
represented by formula  
(III), that the pyridinium ylide moiety pendant from the  
polymer backbone may  
be attached either directly to the backbone (as where m is  
one) or through the  
organic linking group, L (m is two).

The polymeric pyridinium ylides can be used for a  
variety of purposes,  
including treatment and hydrophobization of surfaces.  
Thus, a layer of the  
polymer can be applied from solution to a suitable  
substrate which is then  
subjected to exposure to a source of irradiation sufficient  
to effect the  
desired conversion of the ylide to the corresponding N-acyl  
diazepine. Water  
can be employed and will be a preferred solvent material  
for the preparation of  
a coating composition which can be conveniently applied to  
the substrate by  
spraying, dipping, roll coating or the like. Other  
solvents can, however, be  
used and examples of such solvents are methanol, ethanol  
and trichloromethane.  
A coating composition suited to application to various  
substrate materials will  
typically contain the desired pyridinium ylide polymer in a

concentration of  
about 3 to 4% by weight, although other concentrations can  
be used depending  
upon the particular polymer employed, the nature of the  
solvent utilized, the  
method of application and the nature of the particular  
substrate. Various  
additives such as surfactants, coating aids,  
viscosity-controlling agents, UV  
stabilizers, photoinitiators, triplet sensitizers or the  
like can be included,  
provided that such agents do not interfere with the desired  
conversion of the  
pyridinium ylide compound to the corresponding  
N-acyl-diazepine.

Adhesion of the polymeric image to the wafers was  
evaluated by sticking a  
strip of cellophane tape onto the polymer image; removing  
the tape therefrom;  
and inspecting for evidence of removal of polymer image.  
Inspection showed no  
evidence of such removal.

US-PAT-NO: 6200646

DOCUMENT-IDENTIFIER: US 6200646 B1

TITLE: Method for forming polymeric  
patterns, relief images and  
colored polymeric bodies using  
digital light processing  
technology

----- KWIC -----

Another characteristic of the DMD technology is that it eliminates the need for a contact mask. While contact masks are used for many irradiation applications, there are several drawbacks to using masks. For one thing masks are expensive and time consuming to make, particularly for detailed patterns in which masks must be inspected and repaired before use. Speed and ease of use are also sacrificed when several masks are required. In addition, some polymer properties vary when photopolymerized in the presence of a contact mask, for example light scattering often occurs with masks leading to polymeric patterns of lower resolution, less sharpness and different surface properties.

Second, an application which illustrates the use of this invention to perform a surface modification in a way which is not possible with a typical contact mask procedure is described. A polymer coating is applied to the solid surface of a substrate. Typically this polymer is either hydrophilic or hydrophobic, but can be chemically modified by light activated chemistry. An example of one such system is shown below: ##STR1##

If the DLP technology is applied to this application, then it would be possible to conduct this procedure in fewer steps than is possible with a contact mask (see FIG. 1). As illustrated in FIG. 1A, when a contact mask is used for this application, the process requires at least two steps, first a mask 10 is applied to a polymer surface 12 on a substrate 14 then the irradiation step takes place. This is followed by application of the modifying agent, e.g., by immersing the exposed material in a bath 16 which reacts with the hydrophobic or hydrophilic region. As shown in FIG. 1B, the DLP technology allows the polymer coated substrate 14 to be submerged in a bath 16 which contains the modifying agent. Using DLP technology, the image of the mask can be focused through the modifying agent, assuming the modifying agent does not absorb the irradiation wavelengths, onto the polymer surface 12, so that selective surface modification occurs in the presence of the modifying agent. Attempts to combine these steps in a typical contact mask application results in unacceptable image distortion and loss of resolution because of the inability to focus the image on the polymer surface.

In this example, the colorization of which is based on Scheme 2, a photocolorable photopolymer which turns blue with high light intensity at 400-430 nm was made using CibaTool Stereolithography resin SL 5149 (acrylate) containing 1.0 w % Irgacure 819, 0.35 w % crystal violet lactone (blue color precursor) and 2 w % iodonium salt. A thin film (100 .mu.m) appears colorless to the human eye. A 100 .mu.m thick sample of liquid resin was prepared between glass slides using appropriate spacers. The sample was irradiated with an image from the DLP projector which consisted of four



rectangles, one dark gray, one medium gray, one light gray and one white. The sample was placed under the DLP with a modified optical arrangement and irradiated for 4 minutes. Following irradiation, the polymer was removed from the glass slide. The result was a rectangular polymer which varied in color intensity; such that there was one colorless rectangle which corresponded to the dark gray projection image, a dark blue rectangle which corresponded to the white projection image and two intermediate blue rectangles whose intensity was inversely proportional to the shade of gray in the projected image. The same experiment was repeated using a petri dish of liquid resin at a shorter focal length. In this case a 1.5 minute irradiation produced a 1 mm thick polymer containing series of four differentially colored rectangles with the color properties described above.

US-PAT-NO: 6451141

DOCUMENT-IDENTIFIER: US 6451141 B1

TITLE: Production of seals and coating and  
the bonding of tiles or floor coverings

----- KWIC -----

The invention relates to a method of producing seals and coatings, and of bonding tiles and floor coverings, in which aqueous dispersions containing at least 20% by weight of filler and comprising a polymer mixture of a) an acrylate polymer A having a K value of from 5 to 55 and a glass transition temperature of below -10.degree. C. and b) an acrylate copolymer having a glass transition temperature of from -50 to +50.degree. C., are applied as sealants, coating materials or single-side adhesives. The compositions which are used, based on the filler-containing dispersions of the polymer mixture, are notable in processing for improved fixing in the wet and dry state, high heat stability, good adhesion to rubber and, since they are essentially free from organic solvents, plasticizers and resins, by a high level of environment-friendliness.

The invention relates to methods of producing seals and coatings and of bonding tiles or floor coverings by applying compositions based on aqueous acrylate copolymer dispersions which have a filler content of at least 20% by weight and which are free from major amounts of volatile organic solvents, plasticizers and modified or unmodified natural resins of

low molecular mass.

The invention also relates to the use of such compositions as sealants, coating materials or single-side adhesives (adhesives for one-sided application).

The development of new kinds of polymer dispersions based on acrylate more than 25 years ago saw a significant turning point in the processing of sealants and in the work involved in laying tiles and floor coverings. It was possible to provide the processor with sealants, coating materials or single-side adhesives in whose processing the risks were very greatly reduced relative to the processing of the rubber solutions which had been dominant up to that time, since only 5% rather than 75% of flammable solvents were released. Sealants, and single-side adhesives used for tiles or floor coverings, differ fundamentally from pressure-sensitive adhesives in their use and in the properties which are required for that use. Pressure-sensitive adhesives are, in general, systems having an overall high surface tack and are unfilled systems, i.e. contain no fillers. In contrast to sealants and single-side adhesives they are applied as thin films (film thicknesses of about 20 to 200  $\mu\text{m}$ ) and for this reason alone require very different polymer mechanics. The requirements for single-side adhesives are application of the composition to one side only, and also the ability to correct the laid tiles or floor coverings in the course of processing, the ability to remove fresh residues of composition from the tiles or floor coverings and from the tools using water, and also excellent aging resistance. These special requirements have also led to special test standards, such as the testing of peel and shear strength and the testing of the wet bonding capacity and the dry

gripping capacity.

We have found that this object can be achieved, by applying compositions based on aqueous acrylate copolymer dispersions, containing at least 20% by weight of fillers, as sealants, coating materials (including impregnating materials) or single-side adhesives, if use is made of a filler-containing aqueous dispersion of a polymer mixture comprising a) a polymer A having a K value of from 5 to 55 and a glass transition temperature of below -10.degree. C., containing at least 50% by weight of copolymerized acrylic ester units, and b) a polymer B which is an acrylate copolymer having a glass transition temperature of from -50 to +50.degree. C.

The polymers A can be (prepared in a manner known per se:) for the preparation of polymers A having a very narrow molecular weight distribution ( $M_{sub.w} / M_{sub.n}$  close to 1) a known process of high-temperature polymerization should be employed. (The polymers A are preferably prepared by polymerization in bulk or in solution at from 60 to 220.degree. C. possibly using, for solution polymerization, customary organic solvents) such as hydrocarbons (e.g. toluene), alcohols (e.g. isobutanol), esters (e. g. ethyl acetate) or ketones (e. g. methyl ethyl ketone) with appropriate boiling ranges or establishing the relatively high polymerization temperature in closed reactors under pressure (up to 15 bar) in the case of volatile solvents. The customary polymerization initiators can be employed, in known amounts. In view of the (desired low K values and molecular weights of the polymers A) it is sensible to use polymerization regulators, such as mercaptans, examples of which include mercaptoethanol, mercaptosuccinic acid,

3-mercaptopropyltrimethoxysilane and, in particular, dodecyl mercaptan. (In view of the nature of the use of the polymers A in accordance with the invention it is sensible to carry out extensive removal of volatile impurities such as residual monomers from the polymers A prior to use.)

The filler-containing aqueous formulations with the mixture M comprising the polymers A and B is suitable as a single-side adhesive for floor coverings of, for example, polyvinyl chloride in configurations as multilayer coverings or homogeneous coverings, foam coverings with a textile backing, for example jute, polyester nonwoven, rubber coverings, textile coverings with various backings such as polyurethane foam, styrene-butadiene copolymer foam, a textile secondary backing, needlefelt floor coverings, polyolefin coverings or linoleum coverings, on substrates such as wood, screeding, concrete, ceramic tiles, metal substrates or other suitable substrates.

The aqueous formulation with the polymer mixture used in accordance with the invention can be applied to a substrate using, for example, a toothed applicator. After customary venting, the floor covering is then laid. In terms of processing the novel compositions resemble the solvent-containing single-side adhesives. The compositions used in accordance with the invention feature a good level of performance properties such as peel strength, shear strength, wet bonding capacity and dry gripping capacity and a high heat stability.

The substrates (Glasal 2000 (cement fiber slab) (500.times.200.times.8 mm) and Freudenberg Studio needle-punched web (200.times.50 mm NFC strips)), like

the single-side adhesive, were conditioned under standard climatic conditions (23.degree. C., 50% relative humidity) for 24 hours. Single-sided adhesive is applied using a 2 mm DIN peel knife in the lengthwise direction onto the Glasal 2000 and, after 10 minutes of venting, the needle-punched web coverings (NFC strips) are laid with their reverse side into the bed of adhesive and are pressed on by rolling back and forward 3 times with a 2.5 kg roller. The coverings are peeled off with a stripper at the time intervals indicated, and the increase in the peel resistance in N/5 cm is determined. The rate used for testing is 725 mm/minute. For evaluation, the mean of two test specimens in N/5 cm is formed and the aspect at break is assessed.

The substrates (Glasal 2000 (500.times.200.times.8 mm) and Pegulan B1 test covering (200.times.50 mm)) and the single-side adhesive are conditioned under standard climatic conditions (23.degree. C., 50% relative humidity) for 24 hours. The single-sided adhesive is applied using a 1 mm DIN shear knife in the lengthwise direction to Glasal 2000 and, after 10 to 45 minutes of venting, the PVC is laid with its reverse side into the bed of single-sided adhesive and is pressed on by rolling back and forward 3 times with a 2.5 kg roller. Testing is carried out by peeling with the stripper, and the peel resistance in N/5 cm is determined. The speed used for testing is 725 mm/minute. Evaluation: mean of test specimens in N/5 cm, assessment of aspect at break.

The substrates (Glasal 2000 (60.times.50.times.8 mm) and Pegulan B1 test covering (60.times.50 mm)) and the single-side adhesive are conditioned under standard climatic conditions (23.degree. C., 50% relative humidity) for 24

hours. The single-side adhesive is applied using a 1 mm DIN shear knife in the transverse direction to Glasal 2000. The PVC covering is bonded with the aid of a bonding stencil so as to give a bonding area of 20.times.50 mm. After 5 minutes of venting, the PVC test covering is laid and is pressed on with a manual press and a pressure of 0.3 N/mm.<sup>2</sup> for 10 seconds. After the test specimen has been stored for a period of 14 days under standard climatic conditions, testing takes place in a thermal cabinet at 50.degree. C. under a weight strain of 2 kg (+-.1). Before beginning of testing the test specimens are thermally conditioned for 30 minutes. Evaluation: mean of 5 test specimens in minutes, assessment of aspect at break.

The substrates (Glasal 2000 (150.times.50.times.8 mm) and Pegulan B1 test covering (250.times.50 mm)) and the single-side adhesive are conditioned under standard climatic conditions (23.degree. C., 50% relative humidity) for 24 hours. The single-side adhesive is applied using a 2 mm DIN peel knife in the transverse direction to Glasal 2000. The PVC covering is bonded by its reverse side to the Glasal 2000 in such a way that 3 sides are flush and the covering overhangs on one side. After venting for 10 and 60 minutes the test covering is pressed on with a manual press and a pressure of 0.05 N/mm.<sup>2</sup> for 10 seconds. The test specimen is stored under standard climatic conditions for 14 days and then peeling is carried out, with the speed used for testing being 100 mm/minute. Evaluation: mean of 5 specimens in N/cm; assessment of aspect at break.

1. A method of bonding tiles or floor coverings or both to a substrate, which comprises applying to said substrate an aqueous

acrylate copolymer dispersion having a filler content of at least 20% by weight and which is free from major amounts of organic solvents, plasticizers, and modified or unmodified natural resins of low molecular weight, wherein said aqueous dispersion comprises at least 20% by weight of filler, and of a polymer mixture M, which comprises: a) a polymer A having a K value from 5 to 30 and a glass transition temperature of below -10.degree. C., which is prepared by bulk or solution polymerization and wherein at least 50% by weight of the polymer A comprises co-polymerized units of at least one ester of acrylic acid; and b) a polymer B which is an acrylic co-polymer having a glass transition temperature from -50 to 50.degree. C. and which polymer is prepared by emulsion polymerization and has a number average molecular weight,  $M_{sub.n}$ , of more than 20,000.

11. A method of producing seals or coatings or both on a substrate, which comprises applying to said substrate an aqueous acrylate copolymer dispersion having a filler content of at least 20% by weight and which is free from major amounts of organic solvents, plasticizers, and modified or unmodified natural resins of low molecular weight, wherein said aqueous dispersion comprises at least 20% by weight of filler, and of a polymer mixture M, which comprises: a) a polymer A having a K value from 5 to 30 and a glass transition temperature of below -10.degree. C., which is prepared by bulk or solution polymerization and wherein at least 50% by weight of the polymer A comprises co-polymerized units of at least one ester of acrylic acid; and b) a polymer B which is an acrylic co-polymer having a glass transition temperature from -50 to 50.degree. C. and



which polymer is prepared by emulsion polymerization and has a number average molecular weight,  $M_{sub.n}$ , of more than 20,000.